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Electrical Relaxation in Acid-Form Nafion

by

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Electrical relaxation studies of acid-form NAFION-117 membranes dried in situ at 380K in vacuum have been carried out. Significant electrical conductivity is found and the data are found to be non-Arrhenius. The results are converted to the electrical modulus representation and a conductivity relaxation is observed. A stretched exponential is best-fit to the conductivity relaxation and again, non-Arrhenius behavior is observed for the peak position. Finally, at low temperatures, a new dielectric relaxation peak is found which has an activation enthalpy of about 0.57 eV (13 kcal/mol). This relaxation is analogous to the γ-relaxation observed in mechanical relaxation studies.

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ELECTRICAL RELAXATION IN DRIED ACID-FORM NAFION

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Synopsis

Electrical relaxation studies of acid-form NAFION-117 membranes dried in situ at 380K in vacuum have been carried out. Significant electrical conductivity is found and the data are found to be non-Arrhenius. The results are converted to the electrical modulus representation and a conductivity relaxation is observed. A stretched exponential is best-fit to the conductivity relaxation and again, non-Arrhenius behavior is observed for the peak position. Finally, at low temperatures, a new dielectric relaxation peak is found which has an activation enthalpy of about 0.57 eV (13 kcal/mol). This relaxation is analogous to the γ-relaxation observed in mechanical relaxation studies.

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INTRODUCTION

Perfluorinated ion exchange membranes, such as Nafion, are currently the object of intense interest due to their potential use in fuel cells and other electrochemical applications. The primary interest in these materials stems from the enhanced proton transport due to the presence of water in these membranes. Many studies, including an ongoing effort in this laboratory, have been made aimed at understanding the role of water in proton transport.[1-5] In the present work, complex impedance measurements are carried out on Nafion dried under well-defined conditions. The purpose is to gain new information concerning the polymer, itself. The principal results are the observation and characterization of a previously unobserved electrical relaxation. This relaxation is apparently related to a mechanical relaxation observed in both dry and hydrated films but it previously was not observed dielectrically in hydrated films and was therefore was thought to be dielectrically inactive. In addition, the dried material exhibits significant electrical conductivity. The conductivity and associated conductivity relaxation are found to be non-Arrhenius.

EXPERIMENT

Samples of E. I. du Pont Co. Nafion 117 were obtained from a commercial source. Several samples were studied after different initial treatments. One sample was dried under vacuum at room temperature and another was dried over P_2O_5. One as-received sample was soaked in distilled water and another was soaked after having been dried in vacuum. In addition, as-received samples were studied. Electrical experiments were carried out on these materials and the

results were consistent with those reported previously for similar samples.[4,5] However, all samples were then dried in situ at 380K for about 2 weeks.

It is possible that the microscopic structure of the dried films studied in the present work is somewhat different from that for the as-received or wet films as a result of their being dried at a high temperature. The reason is that Zawodzinski et al.[6] have reported that the ability of Nafion 117 to absorb moisture from water vapor is dependent on the temperature at which the film is dried. They observed that films dried at 378K in a vacuum oven do not reabsorb as much water as films dried at room temperature in either a vacuum oven or over P_2O_5. This change in moisture uptake ability is thought to be due to structural changes in the Nafion films dried at 378K which are likely to involve the declustering of the ionic groups.

Finally, audio frequency values of capacitance, C, and conductance divided by the angular frequency, G/ω, were measured and transformed to the apparent complex dielectric constant, $\varepsilon^*=\varepsilon'-j\varepsilon''$. The procedure is to measure the area, A and the thickness, d, and calculate the value of the real part of the dielectric constant, ε', at room temperature using the usual expression for the capacitance of a parallel plate capacitor:

$$C = \varepsilon_0 \varepsilon' A/d \qquad (1)$$

It was then assumed that the relative change in the real part of the dielectric constant with both frequency and temperature is equal to the relative change in capacitance and hence the effects of thermal expansion have not been included. The imaginary part of the dielectric constant at other frequencies and temperatures was then calculated using the definition:

$$\varepsilon'' = \varepsilon' G/\omega C \qquad (2)$$

where ω is the angular frequency. It is noted that the electrical conductivity, σ, is related to the ε'' via:

$$\sigma = \varepsilon_0 \varepsilon'' \omega \qquad (3)$$

The data were also transformed to the loss tangent:

$$\tan\delta = \varepsilon''/\varepsilon' \qquad (4)$$

and the electric modulus which is defined as:

$$M^* = 1/\varepsilon^* = M' + jM''. \qquad (5)$$

RESULTS AND DISCUSSION

Electrical Conductivity

Typical results for the ac electrical conductivity are shown by the line segments connecting datum points in Fig. 1. Significant dispersion is observed i.e. the value of σ is not constant and so it is useful to determine the effective dc conductivity. This was achieved via complex impedance analysis and a typical complex impedance plot is shown in Fig. 2. It was found that the electrical response is well-represented by a Cole-Cole depressed arc.[7] The Cole-Cole expression:

$$Z^* = \frac{Z_o}{1 + (i\omega\tau_o)^{(1-\alpha)}} \qquad (6)$$

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was best-fit to the data and the effective DC resistance was calculated from the intercept of the depressed arc with the Z' axis. The dimensions of the sample were used to calculate the conductivity from:

$$G = \sigma A/d. \qquad (7)$$

The results are shown by the circles in Fig. 1.

Clearly, significant electrical conductivity is observed. The most likely source of the conductivity is residual water. The existence of a small amount of water remaining in the sample after drying at 380K is consistent with the data of Yeo and Eisenberg.[1] In contradiction, Zawodzinski et al.[8] agree with LaConti et al.[9] that all water is removed at 378K. Of course, it may be that the conductivity observed in the present work is not associated with water, but rather is due to trace impurities.

It is also apparent from Fig. 1 that curvature is observed and consequently the electrical conductivity is non-Arrhenius. This non-Arrhenius behavior suggests that for Nafion dried at 380K the polymer may play an intimate role in proton transport. As a first attempt at understanding the transport mechanism, a VTF[10] equation:

$$\sigma = A' \exp[-E_a'/k(T-T_0')] \qquad (8)$$

was best-fit to the data. The fitting parameters were found to be $\log_{10}(A')=-0.174$ (where A' has units of S/cm), $E_a'=0.180$ eV and $T_0'=227$K.

The values of $\log_{10}(A')$ and T_0' are typical of those which describe the electrical conductivity for anhydrous, amorphous polymer electrolytes.[11,12]

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However, the value of E_a' for Nafion is almost twice as large as for PPO,[12] PDMS-EO[13] or MEEP[14] and is about 50% larger than is observed for amorphous PEO.[15] That is not surprising since the structure and properties of Nafion are significantly different from typical amorphous polymer electrolytes. For example, Nafion 117 dried at about 380K exhibits no clear glass transition.[5] In addition, the poly(tetrafluoroethylene)-like backbone is not flexible at room temperature. Consequently, it is probable that there is a significant difference between the conductivity observed for Nafion dried at 380K and typical ion-conducting polymers. It may be that the sidechains of Nafion 117 are the portion of the polymer intimately involved in the conductivity process. In fact, the electrical conductivity in polymer electrolytes similar in form to Nafion (stiff backbone and flexible sidechains) also exhibit VTF behavior. Typical examples are polystyrene with pendant [oligio(ethylene oxide)]cylclotriphosphazene[16] and N-substituted oligo(ethylene oxide) poly(*p*-phenylene terephthalamide).[17]

Finally, Zawodzinski et al.[6] have carried out ^{1}H NMR measurements in Nafion films of low water content and found that the proton self diffusion coefficients are in reasonable agreement with those calculated from the Nernst-Einstein equation and conductivity data. This agreement is consistent with NMR self-diffusion measurements being reflective of the conductivity process which would rule out proton hopping as the dominant conductivity mechanism in this low water content regime. In Nafion at higher moisture contents[5] and for similar materials,[18] power law behavior (a linear relationship between log σ and log f) is observed which is indicative of hopping behavior. However, as can be deduced from Figs. 1 or 2, power law behavior, and hence hopping conductivity, is not observed in these in-situ dried Nafion which is consistent with the findings of Zawodzinski et al.[6]

Conductivity Relaxation

It is often useful to transform electrical relaxation data for conductive systems to the electric modulus representation.[19] One reason is apparent from Fig. 3 where typical results for ε' vs. temperature for a dry NAFION sample are shown. The associated values of ε'' and $\tan\delta$ are shown in Figs. 4 and 5. It is clear that strong dispersion and apparently large values of ε' are observed at the highest temperatures, beginning at about 300 K for the material dried in situ. The effect is even more pronounced in NAFION containing more water as can be seen in Figs 9a and 9b of the ref. 4, Specifically, strong dispersion was reported beginning at about 150K for wet, and 175K for less wet materials. The rapid, apparent rise in ε' as temperature increases is due to space charge polarization as blocking electrodes have been used. Consequently, the large values of ε' observed at high temperatures do not represent a bulk property of the material. Further discussion of such a false contribution to the dielectric constant is given elsewhere.[20] The primary reason for using the electric modulus formalism is that these large, false values of ε' are suppressed.

Typical data for the imaginary part of the electric modulus are plotted in Figs 6 and 7. Strong peaks are observed which are reminiscent of standard dielectric relaxation and, in fact, are usually referred to as the conductivity relaxation. In an attempt to analyze the data, a theoretical curve based on a stretched exponential decay function:

$$\phi(t) = \exp[-(t/\tau_{SE})^{\beta_{SE}}] \qquad (9)$$

where β_{SE} and τ_{SE} are fitting parameters was best-fit to the data. This equation is usually referred to either as a stretched exponential (SE) or Kohlrausch-Williams-Watts (KWW) distribution function.[21,22] The techniques used in the best-fit

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procedure are given elsewhere[19] and typical best-fit curves are shown in Figure 5. The curves were only best-fit to the central nine datum points, as discussed in ref. 19.

The peak position was determined from each best-fit and plotted vs. reciprocal temperature in Figure 8. The behavior is found to be non-Arrhenius exhibiting slight curvature. For comparison, the data reported elsewhere for "wet" samples were analyzed similarly and are plotted in Figure 9. The data for all three "wet" samples are inconclusive as regards Arrhenius behavior and further work is necessary to properly characterize the temperature dependence of the electrical conductivity in "wet" samples. The uncertainty of their water content with time and temperature is the primary concern since the conductivity data for the unprotected "wet" films were collected in a dewar under vacuum. An effort was made to minimize moisture losses by quenching the films to low temperatures as soon as possible at the outset of the electrical measurements, however, the efficaciousness of these efforts, which will be the focus of a future study, needs to be evaluated by comparison with the electrical properties of films with well-defined water contents which have been hermetically isolated.

The stretched exponential parameter, β_{SE}, for the in-situ dried films was found to vary over the range 0.72 to 0.77 and the increase in β_{SE} with increasing temperature exhibited a rather weak correlation. It is generally accepted that β_{SE} is indicative of the spread in the distribution of conductivity relaxation times with the relaxation behavior approaching single exponential behavior as β_{SE} approaches 1. The large values of β_{SE} determined for the conductivity relaxation of in-situ dried Nafion indicates a rather narrow distribution of relaxation times, especially when one considers that values of β_{SE} for anhydrous poly(propylene oxide) bi-ionic electrolytes are on the order of 0.5.[19] These results are consistent with the ^1H NMR self-diffusion measurements in Nafion 117 films of low water

content by the slow diffusion enhanced pulsed field gradient spin echo technique reported by Zawodzinski et al.[6] Those measurements exhibited only one conponent and hence imply simplicity in the proton conduction mechanism.

γ-Relaxation

It is clear from Fig. 3 that there is also a region of weak dispersion in the dry sample beginning just below 200K. The reason for the dispersion is apparent from Figs. 4 and 5 where a dielectric loss peak is seen. More traditional plots of the data are given in Figures 10 and 11. The peak positions were approximated by inspecting plots similar to Figure 11 at various temperatures and are plotted in Fig. 12. The line shown is the best-fit Arrhenius expression:

$$f_{max}(Hz) = f_o \exp(-E/kT) \qquad (10)$$

From the best-fit, it is found that the preexponential is given by $\log_{10}(f_o)=15.9$ and the activation enthalpy is E=0.57eV (13.2 kcal/mol). This value is midway between the values for the γ-relaxation in the fluoropolymers PTFE, FEP and PFA, for which E is about 16kcal/mol, and ETFE, for which E is about 10.6 kcal/mol.[23] In addition, the position of the loss peak is similar to that for the mechanical loss peak identified as the γ-relaxation. Specifically, Eq. (9) predicts that a 1 Hz dielectric loss peak will be observed at about 181K and Yeo and Eisenberg[1] report that the γ-relaxation is observed mechanically at about 1 Hz and 173K. Further, they report an mechanical loss peak activation energy of about 13 kcal/mole which is in good agreement with the activation enthalpy reported above for the dielectric loss peak. Also, Equation (10) predicts that a 20 Hz dielectric loss peak should occur at about 197K and Starkweather and Chang[2] observe the mechanical γ-relaxation at about 20 Hz and 203K. Consequently, it is clear that the dielectric

relaxation observed in the present work is the γ-relaxation in NAFION 117. This contradicts Yeo and Eisenberg who state that the γ-relaxation is expected to be dielectrically inactive.[1] Of course, the γ-relaxation is only observed in the dry material. It may be rendered inactive by the presence of ions or, more likely, it is probably just masked by the stronger water relaxation and ionic conductivity.

For completeness, a plot of the γ-relaxation in the electric modulus representation is shown in Fig. 13.

CONCLUSIONS

By studying electrical relaxation in Nafion 117 dried at 380K in vacuum, two results have been obtained. First, the electrical conductivity and associated conductivity relaxation has been shown to be non-Arrhenius. Further work will be necessary to reach definite conclusions concerning the temperature dependence of the electrical conductivity in materials containing significant amounts of water. Second, the γ-relaxation has been observed electrically for the first time.

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FIGURE CAPTIONS

Figure 1. Arrhenius plot of the frequency of the electrical conductivity for Nafion 117 dried in situ. The lines are the conductivity determined from Eq. (3) and the circles are the conductivity determined from complex impedance analysis.

Figure 2. Complex impedance plot at 380K for Nafion 117 dried in situ. The solid line is the best-fit Cole-Cole depressed arc. The triangle is the center of the circle.

Figure 3. Real part of the dielectric constant vs. temperature at three frequencies for Nafion 117 dried in situ. Straight line segments connect the datum points.

Figure 4. Imaginary part of the dielectric constant vs. temperature at three frequencies for Nafion 117 dried in situ. Straight line segments connect the datum points.

Figure 5. tanδ vs. temperature at three frequencies for Nafion 117 dried in situ. Straight line segments connect the datum points.

Figure 6. Imaginary part of the electric modulus vs. temperature at four frequencies for Nafion 117 dried in situ. The frequencies are: a-10 Hz, b-10^2Hz, c-10^3Hz, d-10^4Hz, and e-10^5Hz. Straight line segments connect the datum points.

Figure 7. Imaginary part of the electric modulus vs. frequency at two temperatures for Nafion 117 dried in situ. The solid curves are the best-fit strĕtched exponential based on Equation (9).

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Figure 8. Arrhenius plot of the frequency of the peak maximum for the conductivity relaxation for Nafion 117 dried in situ.

Figure 9. Arrhenius plot of the frequency of the peak maximum for the conductivity relaxation for Nafion 117 containing significant amounts of water. The plots are for the materials studied in reference 1 which are from left to right: (a) nominally dry, (b) as-received and (c) soaked in distilled water.

Figure 10. Imaginary part of the dielectric constant vs. temperature at five frequencies for Nafion 117 dried in situ. Straight line segments connect the datum points.

Figure 11. Imaginary part of the dielectric constant vs. frequency at three temperatures for Nafion 117 dried in situ.

Figure 12. Arrhenius plot of the frequency of the peak maximum for the γ-relaxation for Nafion 117 dried in situ.

Figure 13. Imaginary part of the electric modulus vs. temperature at three frequencies for Nafion 117 dried in situ. Straight line segments connect the datum points.

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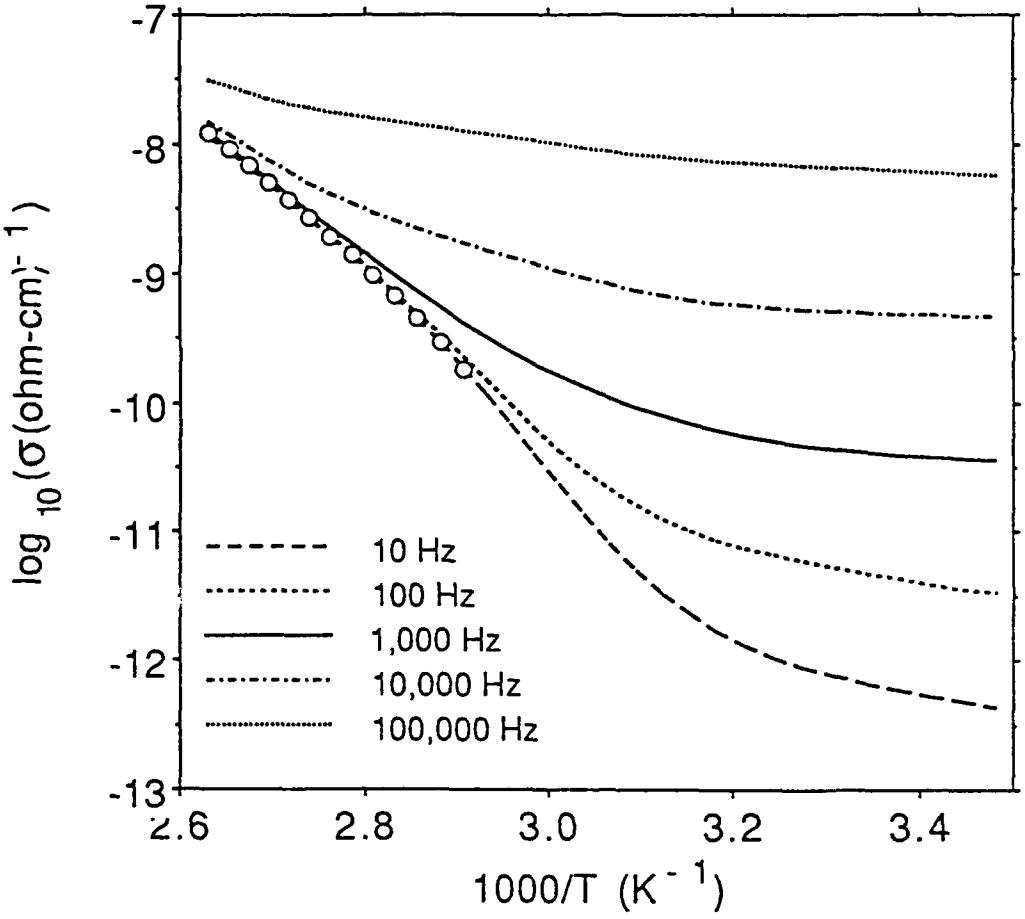

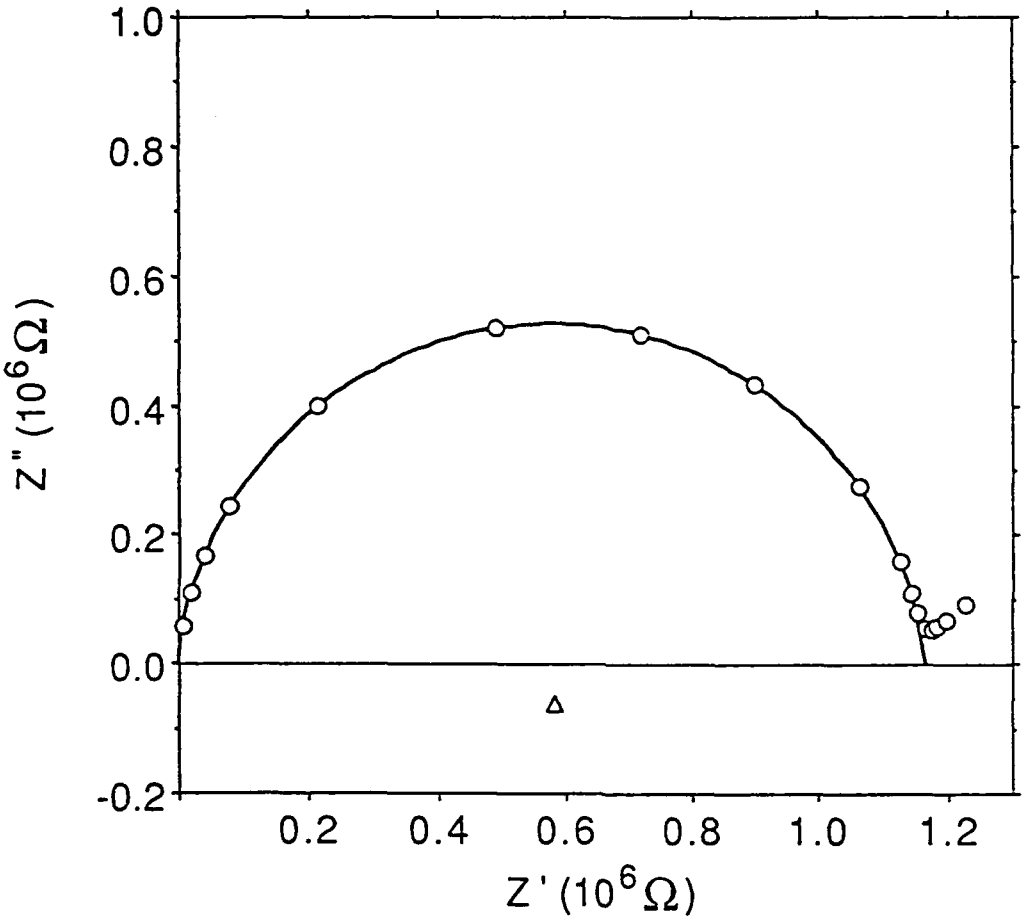
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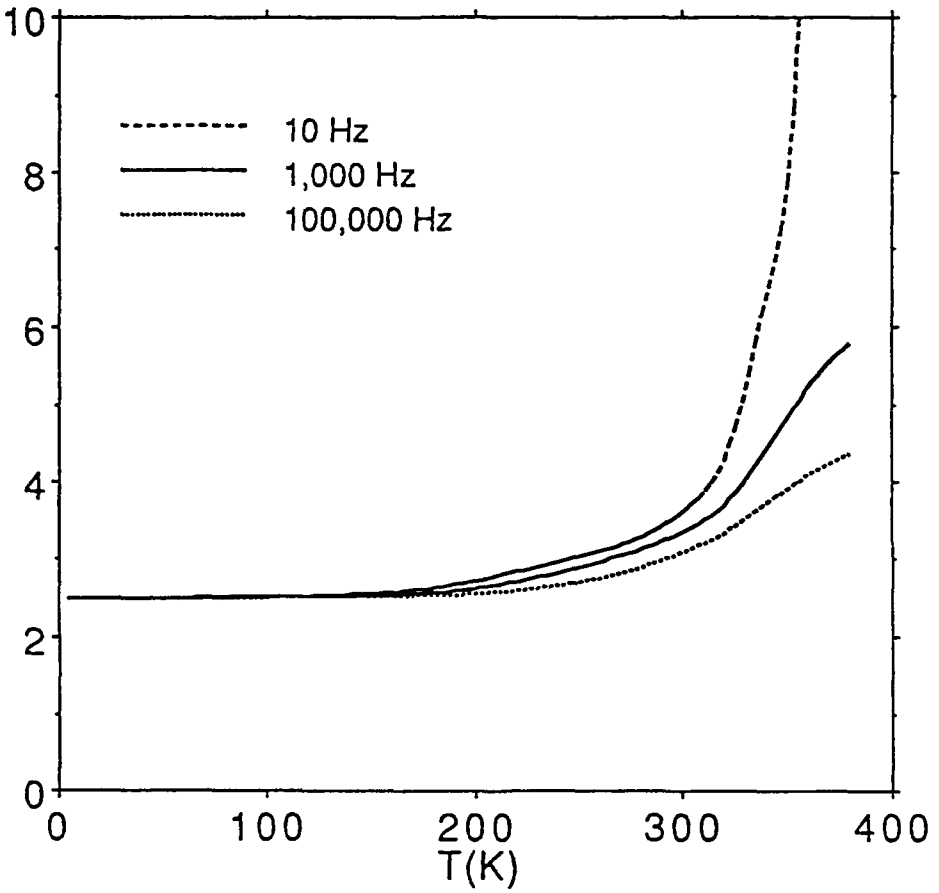

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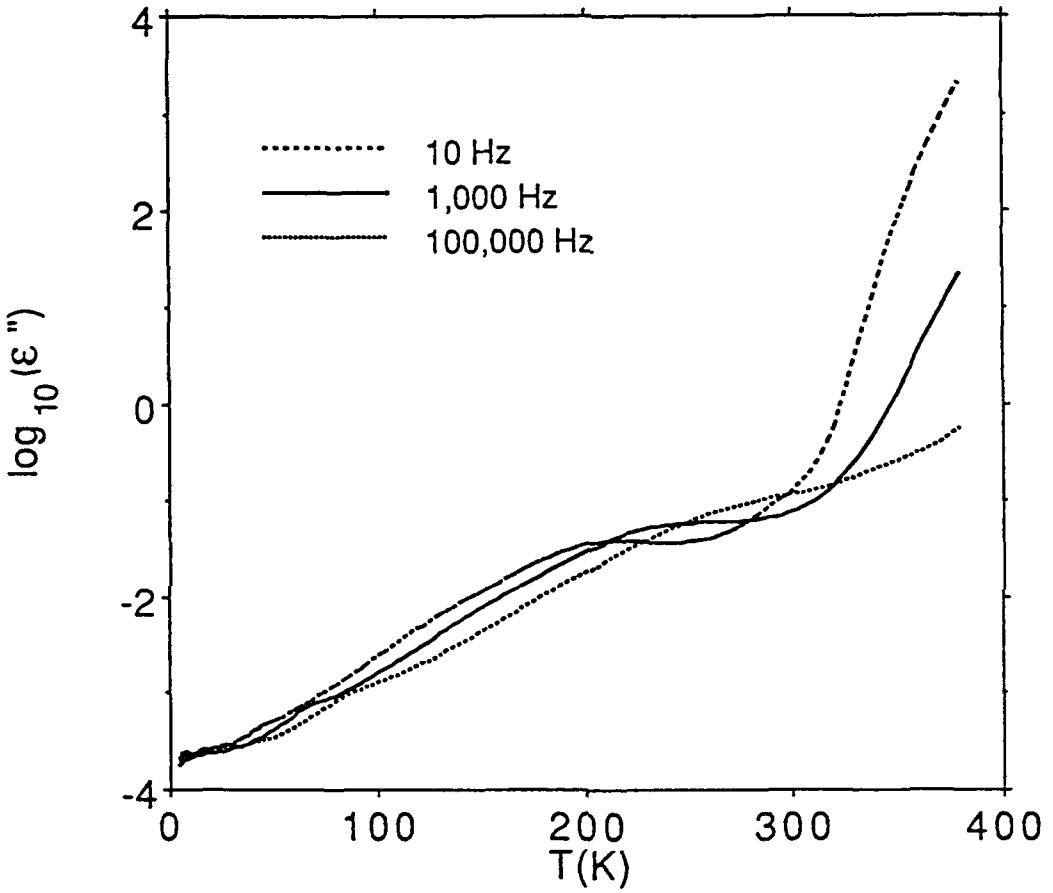

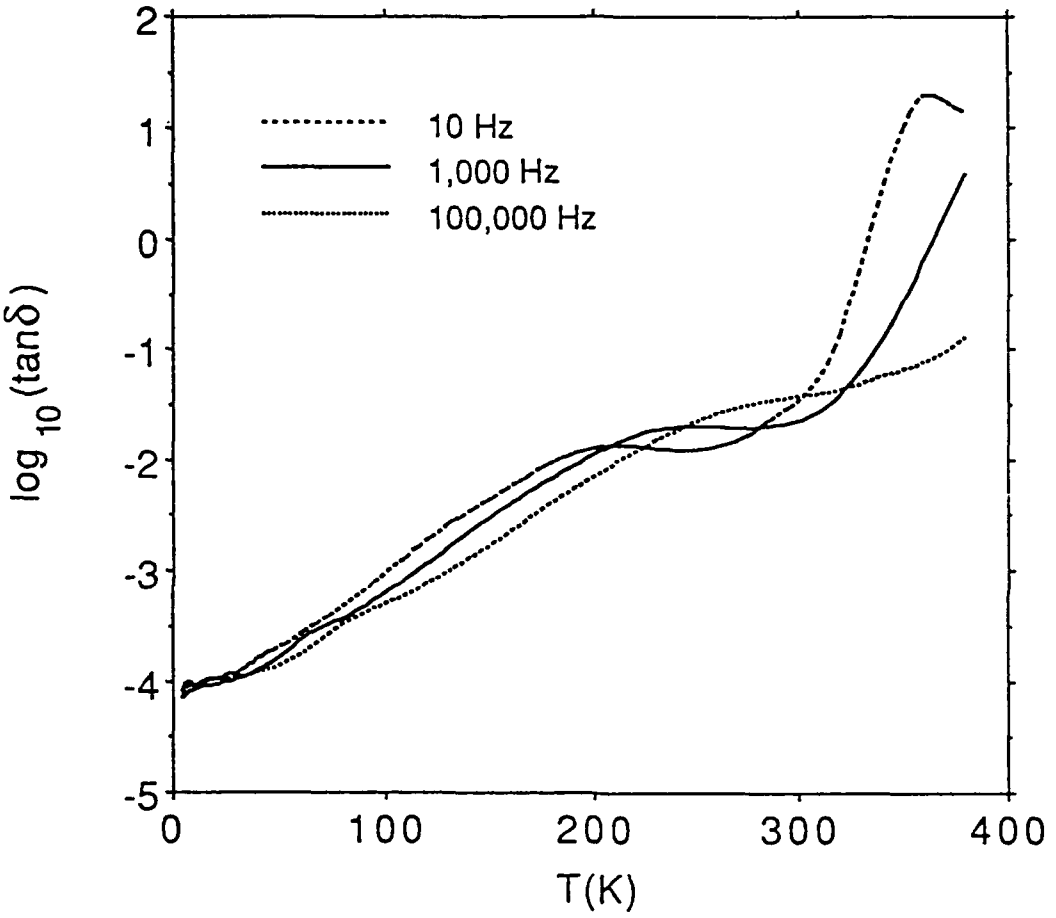
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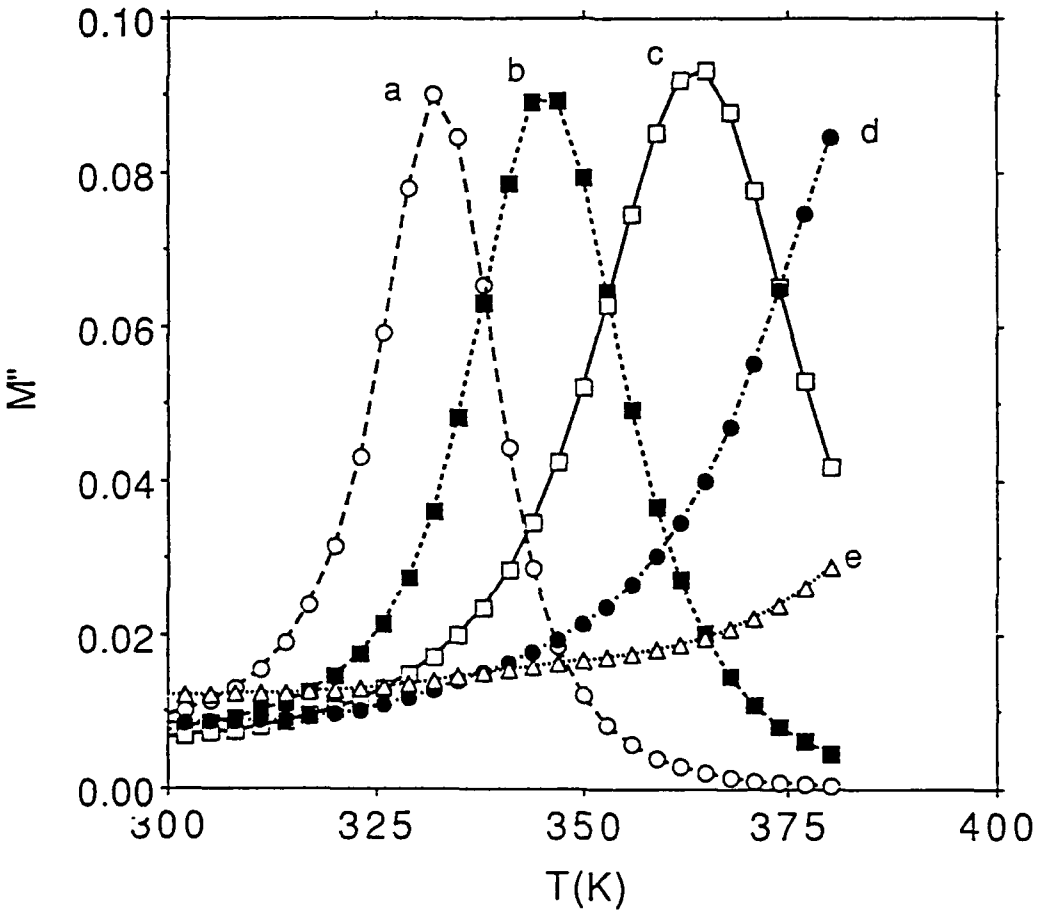

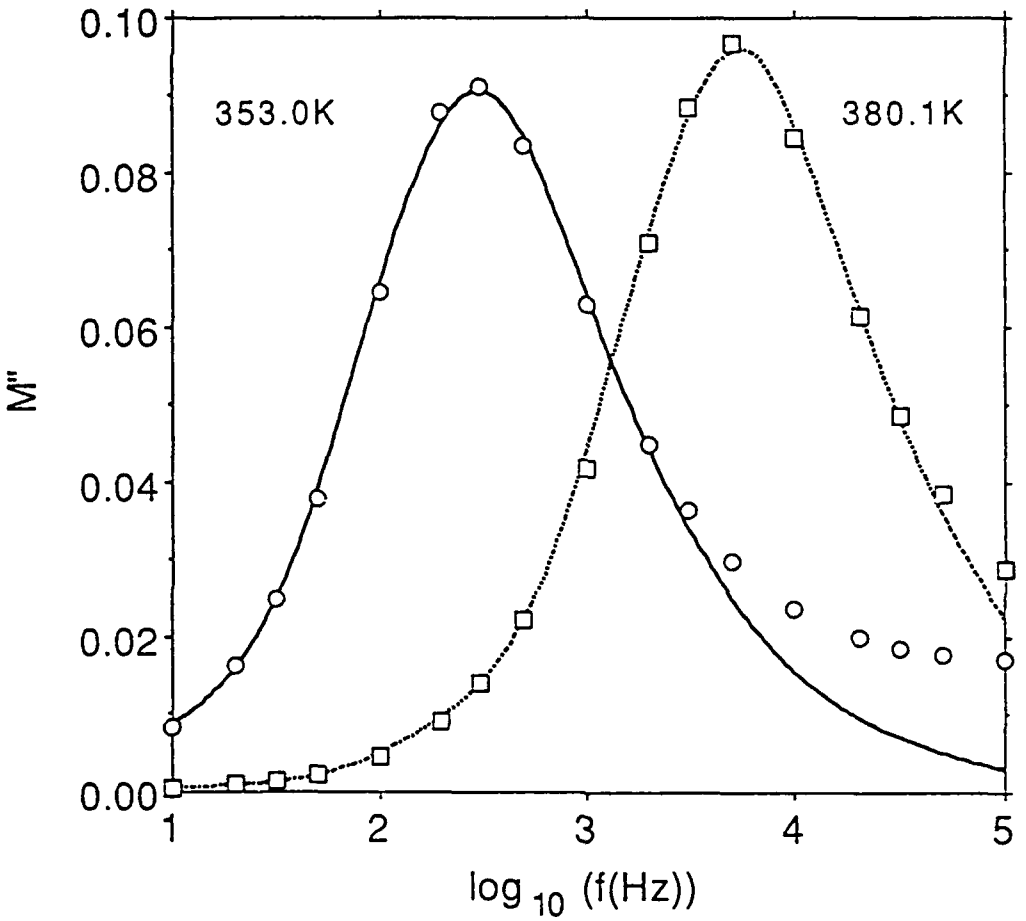
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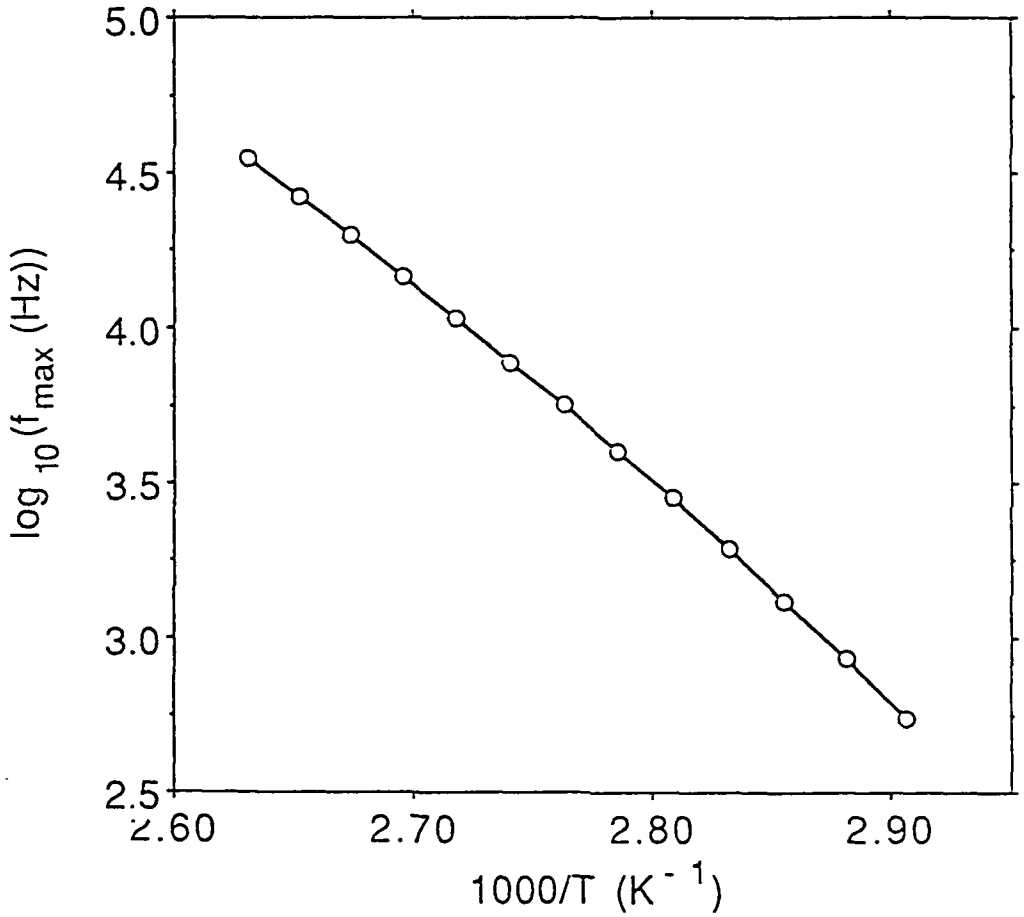
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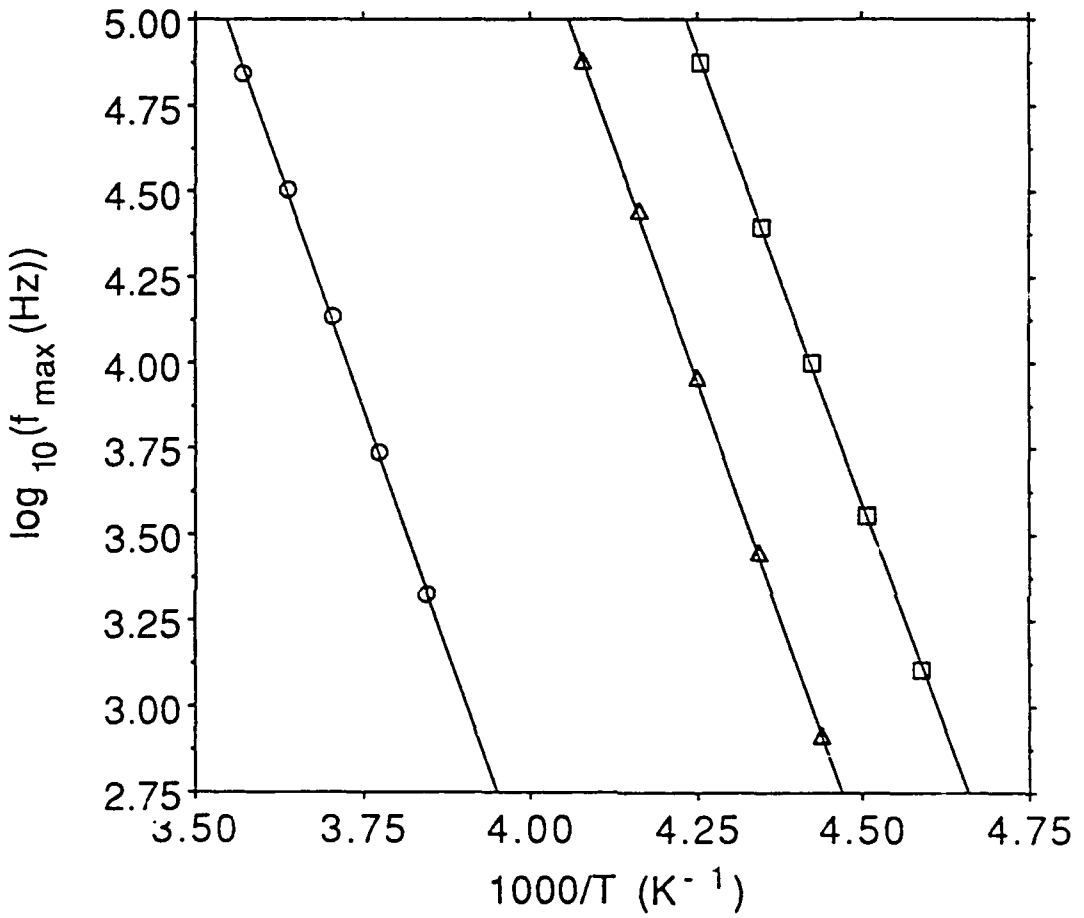
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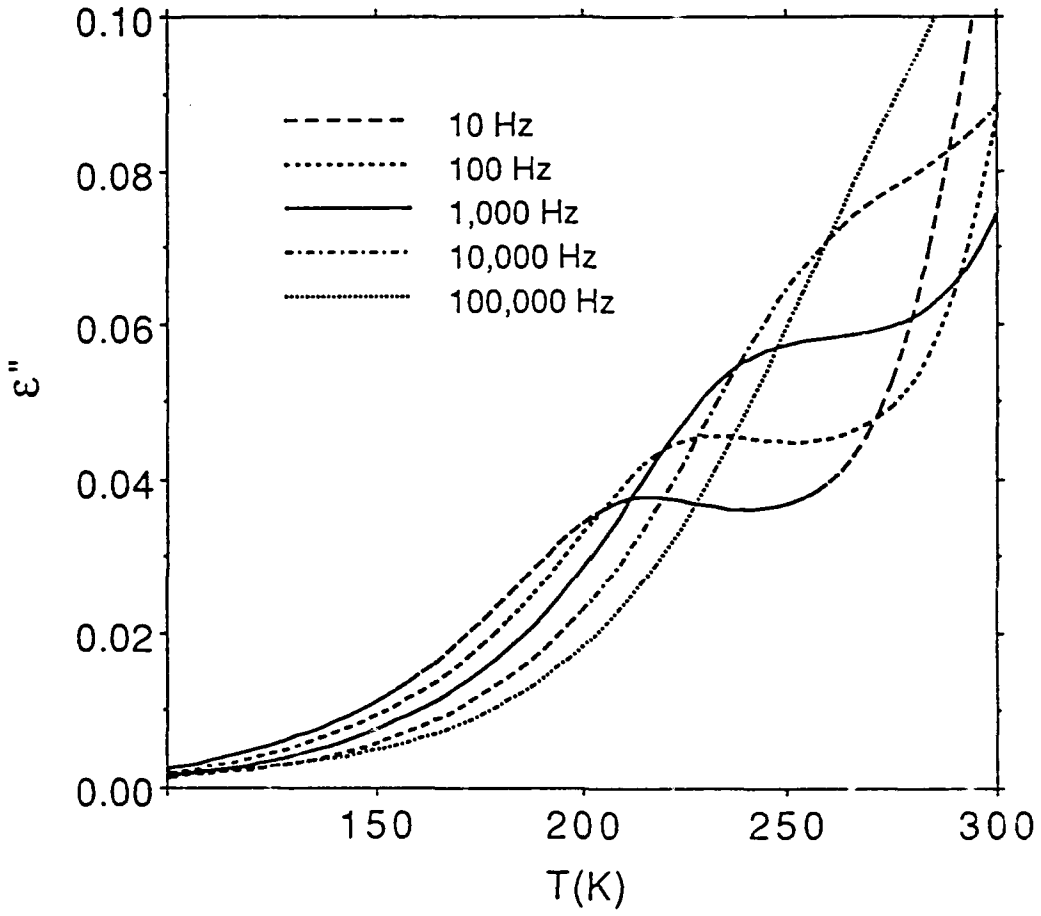
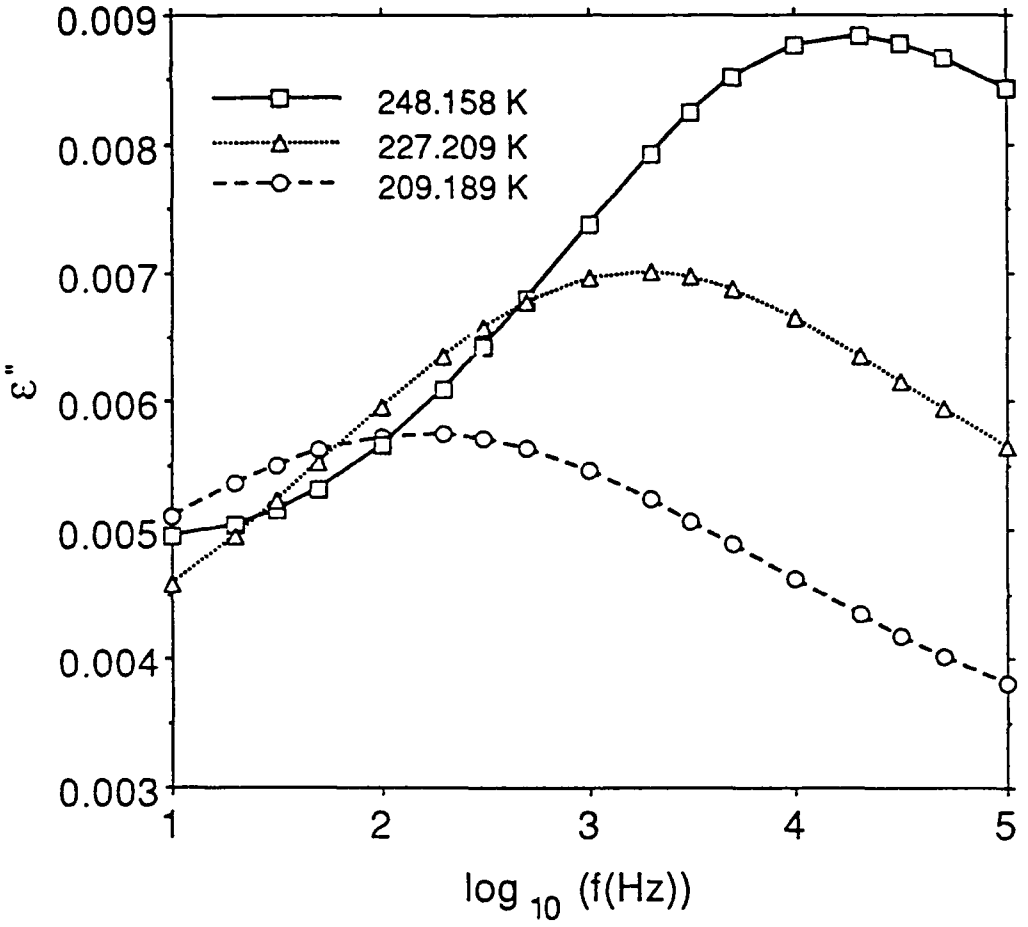
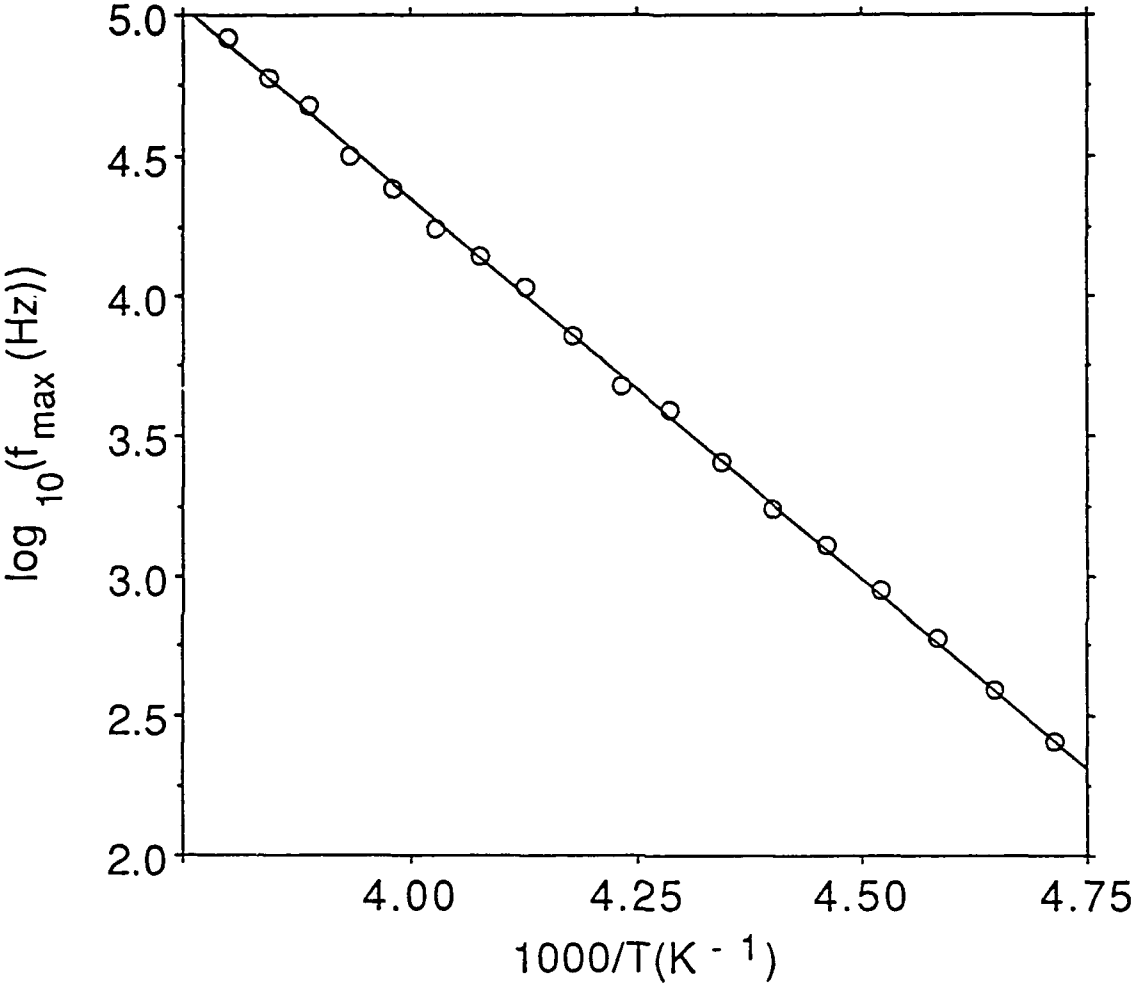
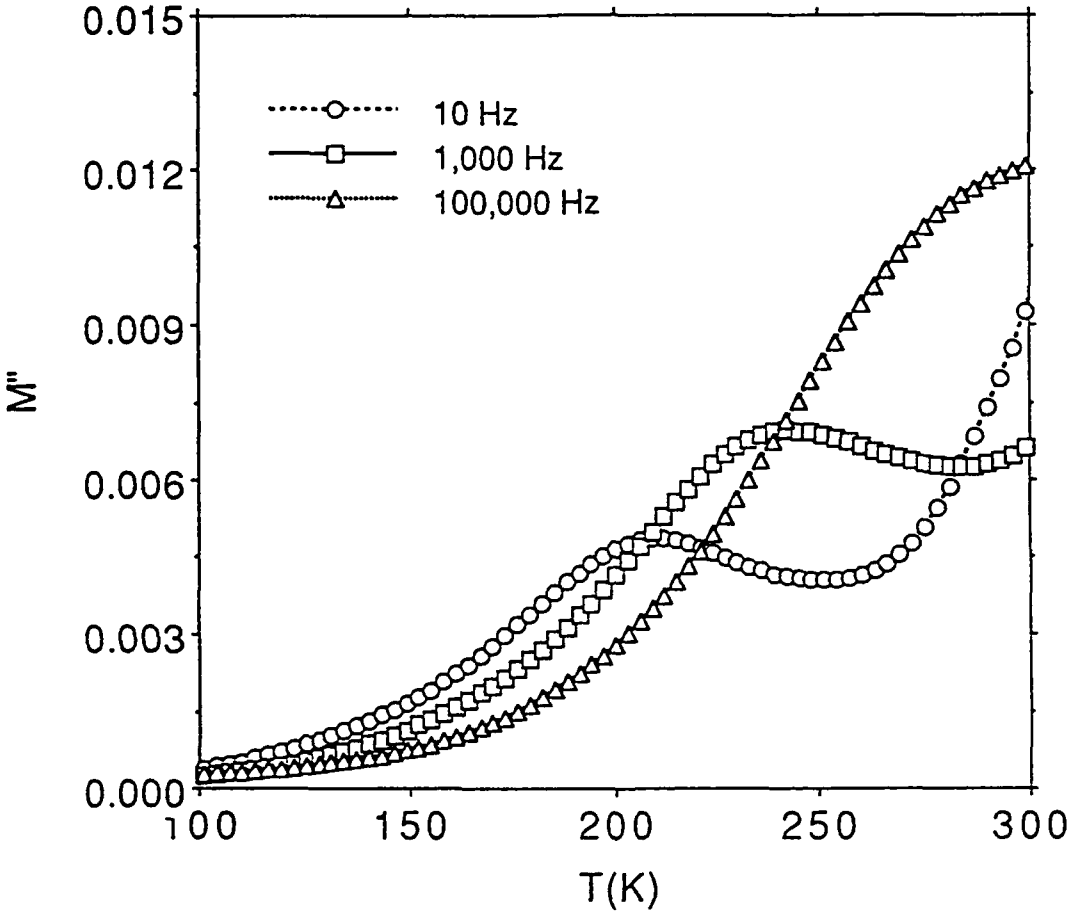


REPRODUCED AT GOVERNMENT EXPENSE




5.0
4.5
4.0
3.5
3.0
2.5
2.0
log 10(fmax (Hz))
4.00
4.25
4.50
4.75
1000/T(K - 1)

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